

A comparative study of O₃ formation in the Houston urban and industrial plumes during the 2000 Texas Air Quality Study

P. H. Daum,¹ L. I. Kleinman,¹ S. R. Springston,¹ L. J. Nunnermacker,¹ Y.-N. Lee,¹ J. Weinstein-Lloyd,² J. Zheng,³ and C. M. Berkowitz⁴

Received 2 March 2003; revised 18 July 2003; accepted 5 August 2003; published 2 December 2003.

[1] Ozone formation in the Houston area during a period of high ozone concentrations that occurred on 29 August 2000 during the TexAQS 2000 study is examined to understand differences in the sources of O₃ precursors and the rate and efficiency of ozone formation over the city of Houston and the industrialized Ship Channel region to the east of Houston. From late morning through late afternoon on 29 August, a period of stagnation occurred, allowing accumulation of O₃ and product species separately over downtown Houston and the Houston Ship Channel. Three aircraft flights were made in the region, starting from about 0900 CST and extending to about 1700 CST. A localized plume of high O₃ ranging between 120 and 200 ppb was observed over the Ship Channel on all of these aircraft flights. Over the same time period, O₃ concentrations over the city were much lower ranging between 40 and 90 ppb. NO_x concentrations measured in the two regions in the late morning were roughly the same, but hydrocarbon reactivities over the industrial area were much higher, by as much as a factor of 10. Photochemical box model calculations constrained by observations of NO_x, hydrocarbons, O₃, and other stable species indicated that the instantaneous ozone formation rate was much lower (3–18 ppb/h) over downtown Houston than it was over the Ship Channel (3–80 ppb/h). The much faster O₃ formation rates and higher concentrations observed over the Ship Channel are attributed to the much higher hydrocarbon reactivity, the majority of which was contributed by low molecular weight alkenes. These high hydrocarbon reactivities also caused O₃ over the Ship Channel to be produced with much higher efficiency than over urban Houston. Comparison of photochemical product distributions suggests that O₃ formation in the urban area is much more hydrocarbon limited than in the Ship Channel, consistent with the geographic distribution of major hydrocarbon sources in the area.

INDEX TERMS: 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry; **KEYWORDS:** urban pollution, ozone formation, industrial hydrocarbons

Citation: Daum, P. H., L. I. Kleinman, S. R. Springston, L. J. Nunnermacker, Y.-N. Lee, J. Weinstein-Lloyd, J. Zheng, and C. M. Berkowitz, A comparative study of O₃ formation in the Houston urban and industrial plumes during the 2000 Texas Air Quality Study, *J. Geophys. Res.*, 108(D23), 4715, doi:10.1029/2003JD003552, 2003.

1. Introduction

[2] A primary objective of the 2000 Texas Air Quality Study (TexAQS 2000) was to examine the effects of different sources of ozone precursors on the occurrence of ozone episodes in and around Houston, TX. In addition to

the usual sources of ozone precursors originating from on- and off-road vehicles, stationary sources, such as fossil-fueled electrical power plants, and vegetation; Houston is unique among U.S. cities in that it is also home to one of the largest concentrations of petrochemical industries in the world. These industrial facilities are spread throughout southeast Texas, but the highest density is located in the region surrounding the Houston Ship Channel, which extends from the northernmost reaches of Galveston Bay to the eastern edge of the city of Houston, a distance of some 30 km.

[3] It is believed that emissions from the industries surrounding Houston have a major role in the occurrence of exceedances of the 1-hour, 120-ppb National Ambient Air Quality Standard for ozone. The character of these episodes is typically much different than that observed in

¹Environmental Sciences Department, Atmospheric Sciences Division, Brookhaven National Laboratory, Upton, New York, USA.

²Chemistry/Physics Department, State University of New York at Old Westbury, Old Westbury, New York, USA.

³Institute for Terrestrial and Planetary Atmospheres, State University of New York at Stony Brook, New York, USA.

⁴Atmospheric Sciences and Global Change Division, Pacific Northwest National Laboratory, Richland, Washington, USA.

other areas of the country in that frequently only a small region is affected by an extremely high concentration of ozone (peak concentrations >200 ppb) that occurs for only a relatively short period of time. This differs, for example, from ozone episodes in the eastern United States, where high ozone tends to occur over relatively large areas and values >120 ppb can persist for much longer periods of time. The local character of these episodes combined with the typical short duration of high ozone concentrations suggests that the ozone originates from a geographically constrained region of sources emitting high-reactivity hydrocarbons, most likely those surrounding the Houston Ship Channel [Kleinman *et al.*, 2002; Ryerson *et al.*, 2003].

[4] In several other publications presenting results from the TexAQS 2000 study, O₃ formation was examined under flow conditions where plumes from the major source regions in the region (City of Houston, Houston Ship Channel, and the Parrish Power Plant) could be studied separately [Ryerson *et al.*, 2003] and where the Houston urban and Ship Channel plumes were combined [Wert *et al.*, 2003]. The Ryerson *et al.* [2003] study noted significant differences in both the rate and efficiency of O₃ formation in plumes from these sources. Ozone formation was slow and inefficient in the Parrish Power Plant Plume, somewhat faster and more efficient in the Houston urban plume, and very fast and efficient in the composite Houston Ship Channel Plume. These differences in rates and efficiencies were attributed to large differences in the Volatile Organic Compounds (VOC) to NO₂, OH reactivity ratio (hereinafter referred to as the VOC/NO₂ reactivity ratio) in the sources from which these plumes originated. The Parrish Power Plant emits NO_x, but little if any hydrocarbons, making the VOC/NO₂ reactivity ratio in the plume very low and requiring the admixture of ambient air containing hydrocarbons to form O₃. Similar to most urban areas in the United States, emissions from Houston itself originate primarily from mobile sources and for this reason exhibit a fairly low VOC/NO₂ reactivity ratio, which limits the rate and efficiency with which O₃ is formed. In contrast, emissions from the Houston Ship Channel were found to have VOC/NO₂ reactivity ratios that were many times higher than urban Houston, conditions which promoted the rapid and efficient formation of high concentrations of O₃. In the Wert *et al.* [2003] study, the combined Houston urban and Ship Channel emissions rapidly and efficiently produced an O₃ plume with concentrations in excess of 200 ppb. It was concluded that measured concentrations of ethene and propene emitted from the Ship Channel could alone account for the high concentrations of both O₃ and formaldehyde that were observed.

[5] In this paper we examine data collected at the surface and by aircraft on 29 August 2000, a day when a relatively long period of stagnation occurred during most of the daylight hours, allowing the separate accumulation of O₃ and O₃ precursors over downtown Houston and the Ship Channel. Ozone concentrations over the Ship Channel rose to values in excess of 200 ppb by late afternoon but over the city remained below 100 ppb. A sea breeze transported ozone accumulated in the Ship Channel to the NNW late in the afternoon, causing a few of the surface stations on the east side of Houston to experience transient exceedance of the (U.S.) national ambient air quality standard (NAAQS)

for O₃. Examination of this data provides insight into the sources of O₃ precursors in each of these regions and of differences in the rate and efficiency of O₃ formation. Many of the general features of O₃ formation observed in the Houston area during the entire TexAQS 2000 experiment are well illustrated by the data collected on 29 August 2000.

2. Experimental

[6] TexAQS 2000 was focused on southeast Texas in the area surrounding Houston. Figure 1 shows a map of the project area. The symbols indicate measurement sites that were active during the program. The light blue symbols indicate network sites sponsored by a variety of organizations that monitor some component of Houston air quality, and the boldface symbols are special sites that were set up for the TexAQS 2000 program. Sites labeled GC/ARCH were part of a special sampling network set up under Environmental Protection Agency's (EPA) support to examine aerosols emanating from Ship Channel sources. Details regarding measurements made at these special sites will be discussed elsewhere. Downtown Houston is located within the center of the rectangular set of roads in the middle of the map. The Houston Ship Channel extends from the east side of Houston to Galveston Bay and serves as a conduit for the shipping of raw materials and products from industries in the area, many located close to the Ship Channel.

2.1. Meteorology

[7] Early on 29 August a strong high-pressure center was located just to the east of Houston, causing weak winds from the southeast both at the surface and aloft. As the high moved offshore and passed south of Houston, winds became very weak from the SSW, causing emissions from Houston and the industries surrounding the Ship Channel to be transported very slowly to the ENE. Winds were nearly stagnant throughout the middle portion of the day, but during the late afternoon a sea breeze developed causing the accumulated emissions from the Ship Channel to be advected to the north and northwest by early evening. Surface temperatures by early afternoon exceeded 35°C throughout most of the area, skies were generally clear, and no precipitation was observed in the area.

2.2. Trace Gas and Aerosol Measurements

[8] Oxides of nitrogen were measured using a three-channel NO/O₃ chemiluminescence instrument as described by Nunnermacker *et al.* [1998] except with the molybdenum converter mounted external to aircraft to minimize inlet losses of NO_y. Sample air was admitted to the converter through a small opening (~1 mm) set perpendicular to the motion of the aircraft. A separate perfluoroalkoxy (PFA) Teflon lined inlet was used to sample NO and NO₂. Instrument response was determined by multipoint calibrations on the ground and in-flight standard additions. The efficiencies of the photolytic NO₂ converter and the molybdenum NO_y converter averaged 34.6% $s = 0.9\%$, and 99.6% $s = 0.3\%$, respectively. On the basis of variations of in-flight zeroes and standard additions, the uncertainty in the NO concentrations for 10-s averaged data is estimated to be 20 ppt $\pm 10\%$ of the NO concentration, 100 ppt $\pm 15\%$ of the NO₂ concentration, and 250 ppt $\pm 10\%$ of the NO_y concentration. The sampling

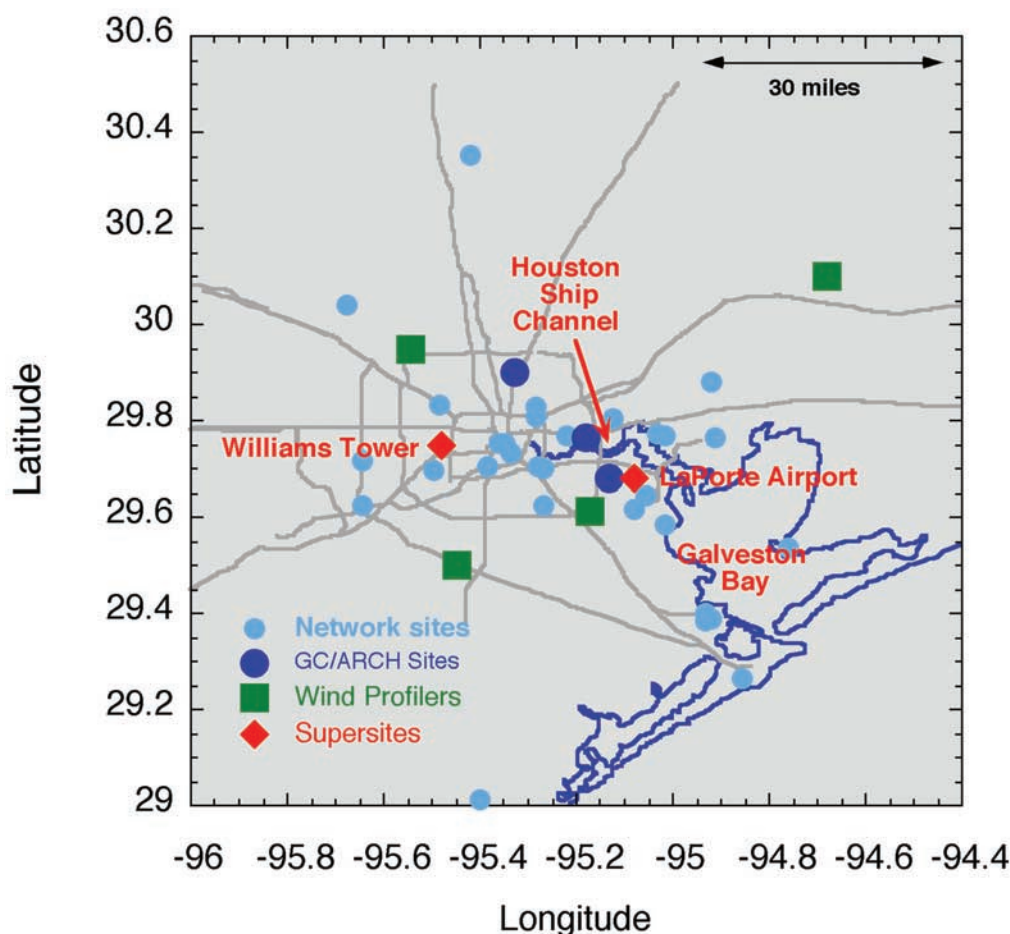


Figure 1. Map of project area showing measurement sites and geography of the area around Houston, TX. Sites contributing to measurements for the program are indicated by the various symbols on the map. Sites labeled GC/ARCH were funded by EPA to examine aerosol emanating from Ship Channel sources. The sites at LaPorte Airport and Williams Tower were special sites set up for the duration of the study. The remaining sites were network sites maintained by various organizations to monitor Houston air quality.

efficiency of the NO_y inlet for HNO₃ was not measured in flight. However, study of a power plant plume during the TexAQS 2000 study showed that NO_y was conserved relative to SO₂ as the plume aged and NO₂ was converted to HNO₃ [Springston *et al.*, 2002]. Validity of the NO₂ measurements on 29 August was confirmed by comparing the quantity NO₂ + O₃ in a fresh plume in which O₃ had been titrated to O₃ concentrations measured adjacent to the plume. Concentrations agreed to within about 10%.

[9] O₃ was measured using a UV absorption detector (Thermo Environmental Instruments, Model 49–100). The O₃ detector was calibrated by gas phase titration of a diluted National Institute of Standards and Technology's (NIST) NO standard. In-flight zeroes were obtained using a charcoal trap to remove ambient O₃. The estimated uncertainty in the O₃ concentration is 5 ppbv ± 5% of the measured concentration. Sulfur dioxide concentrations were measured using a modified commercial fluorometric instrument (Thermo Environmental Instruments, Model 43-S); modifications have been described elsewhere [Nunnermacker *et al.*, 1998]. Both calibrations and in-flight standard additions were performed with a certified gas-phase standard. Estimated uncertainty is 200 ppt ± 10% of the measured

concentration. CO measurements were made with a modified nondispersive infrared detector (Thermo Environmental Instruments, Model 48). Calibrations were performed by serial dilution of a NIST CO standard. In-flight zeroes were performed using hopcolite to remove CO from the sample air. Estimated uncertainty in the CO concentrations is 50 ppb ± 15% of the measured concentration. Peroxides were measured by scrubbing followed by derivitization and fluorescent detection [Weinstein-Lloyd *et al.*, 1998]. Uncertainty for total peroxides is estimated to be ±15%. Formaldehyde was measured by aqueous scrubbing and chemical derivitization followed by high-performance liquid chromatography (HPLC) separation and UV-Vis detection. Measurement uncertainty was estimated to be ±12% [Lee *et al.*, 1998] on the basis of calibrations using aqueous phase standards; inlet losses, if any, are unknown. Hydrocarbons were measured by canister collection followed by GC/FID separation and detection [Rudolph and Khedeim, 1985; Rudolph, 1999]. O₃ measurements on the Twin Otter reported here were made using a UV absorption detector (Thermo Environmental Instruments, Model 49–100); hydrocarbons were measured by canister collection followed by GC/FID [Harley *et al.*, 2001].

2.3. Aircraft Flights

[10] Four aircraft flights were made on 29 August, two by the Baylor Twin Otter, and two by the DOE G-1 aircraft. The morning and afternoon G-1 flights and the afternoon flight of the Twin Otter will be discussed here. Ground tracks for the three flights are shown in Figures 2a–2c. All three flights included segments over downtown Houston, the Houston Ship Channel just to the east of downtown Houston, as well as the areas surrounding these locations. The first G-1 flight commenced at 0830 CST and ended at about 1130 CST; the second G-1 flight extended from 1300 CST to 1600 CST. The midday Twin Otter flight (1100–1400 CST) overlapped the two flights of the G-1. With the exception of several vertical profiles conducted by each of the aircraft, these flights were made in the lower part of the boundary layer at altitudes principally between 500 and 750 m, msl.

3. Results

3.1. Geographic Distribution of O₃, O₃ Precursors, and Intermediate Species

3.1.1. Surface Ozone Concentrations

[11] Regional ozone concentrations measured at the surface on the morning of 29 August were very low by Houston standards (Figure 3). At many of the sites, particularly those south of Houston, concentrations were 20–30 ppb due to the generally southerly winds that brought relatively clean Gulf air to the region. Regional O₃ concentrations increased throughout the day to 60–80 ppb, depending on location. A localized area of relatively high ozone began to form just east of the Ship Channel by late morning. This region of relatively high ozone spread to sites on the northeast side of the city. During the late afternoon a sea breeze developed, transporting ozone that had been formed in and around the Ship Channel to the NNW (see the panels labeled 1400, 1600, and 1800 in Figure 3). The highest 1-hour average ozone concentration of 146 ppb was observed at a site north of the Ship Channel in the late afternoon (Figure 3).

3.1.2. Aircraft Measurements

[12] Ground tracks for the three aircraft flights coded for the O₃ concentration are shown in Figure 2. For some segments of the flights, the aircraft flew over the same track multiple times. The graphs present data so that the highest O₃ concentrations with larger symbols are overlaid by lower concentrations with smaller symbols. Ozone concentrations for most of the region over which the flights were made remained at modest levels (<80 ppb) throughout the day. Although it is not apparent from the way the data are plotted, O₃ concentrations for the morning flight away from the Ship Channel were in fact quite a bit lower than 80 ppb, for the most part ranging between 30 and 40 ppb, similar to the surface observations shown in Figure 3.

[13] During the morning G-1 flight the only region to exhibit elevated O₃ concentrations was around the Houston Ship Channel (Figure 2a). Parts of this area were sampled as early as 0900 CST, and even at that early hour ozone concentrations of 80 ppb, 30–40 ppb in excess of regional background, were observed. Toward the end of the morning flight, a well-developed O₃ plume exhibiting a peak O₃ concentration of 150 ppb was observed east of downtown Houston and just to the north of the Ship Channel and Galveston Bay.

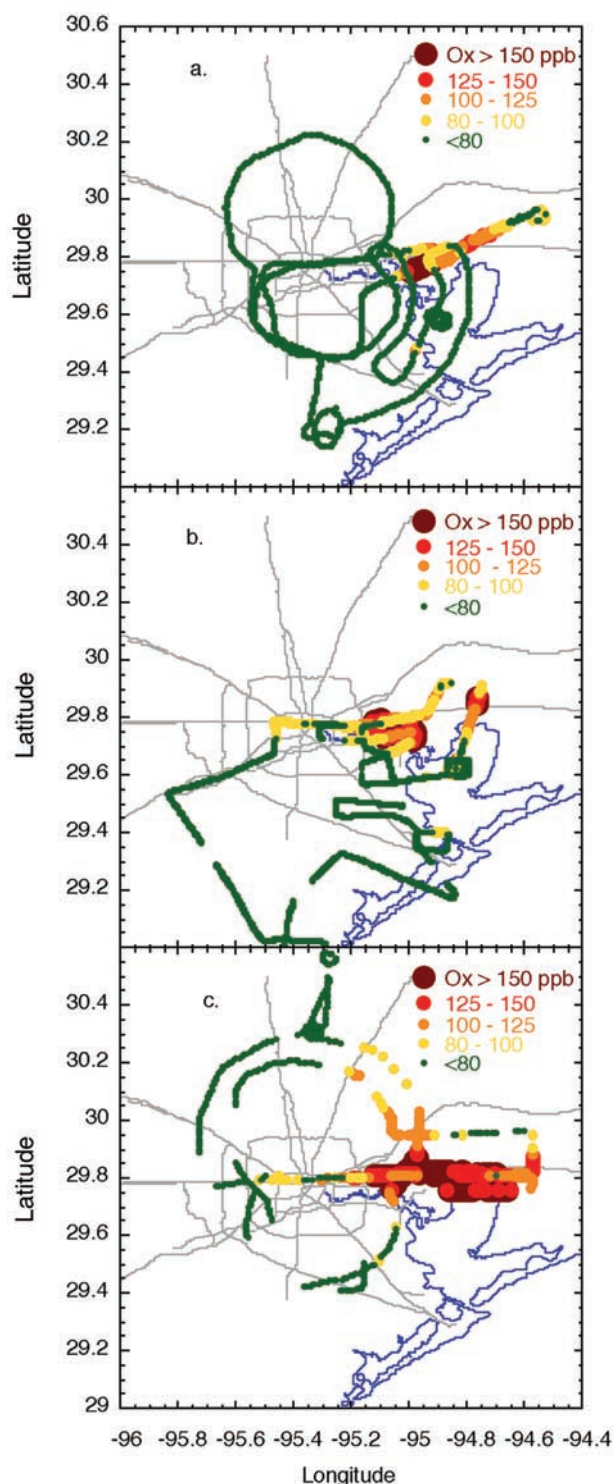


Figure 2. Ground tracks for the three aircraft flights made on 29 August 2000. Measured ozone concentrations are indicated by the size and color of the symbols on the tracks. (a) Indicates the ground track of the morning flight of the G-1, (b) indicates the ground track of the midday Twin Otter Flight, and (c) indicates the ground track of the afternoon G-1 flight. Note the accumulation of O₃ in the region east of downtown Houston throughout the day. Gaps in the data are caused by instrument zeroes or calibrations.

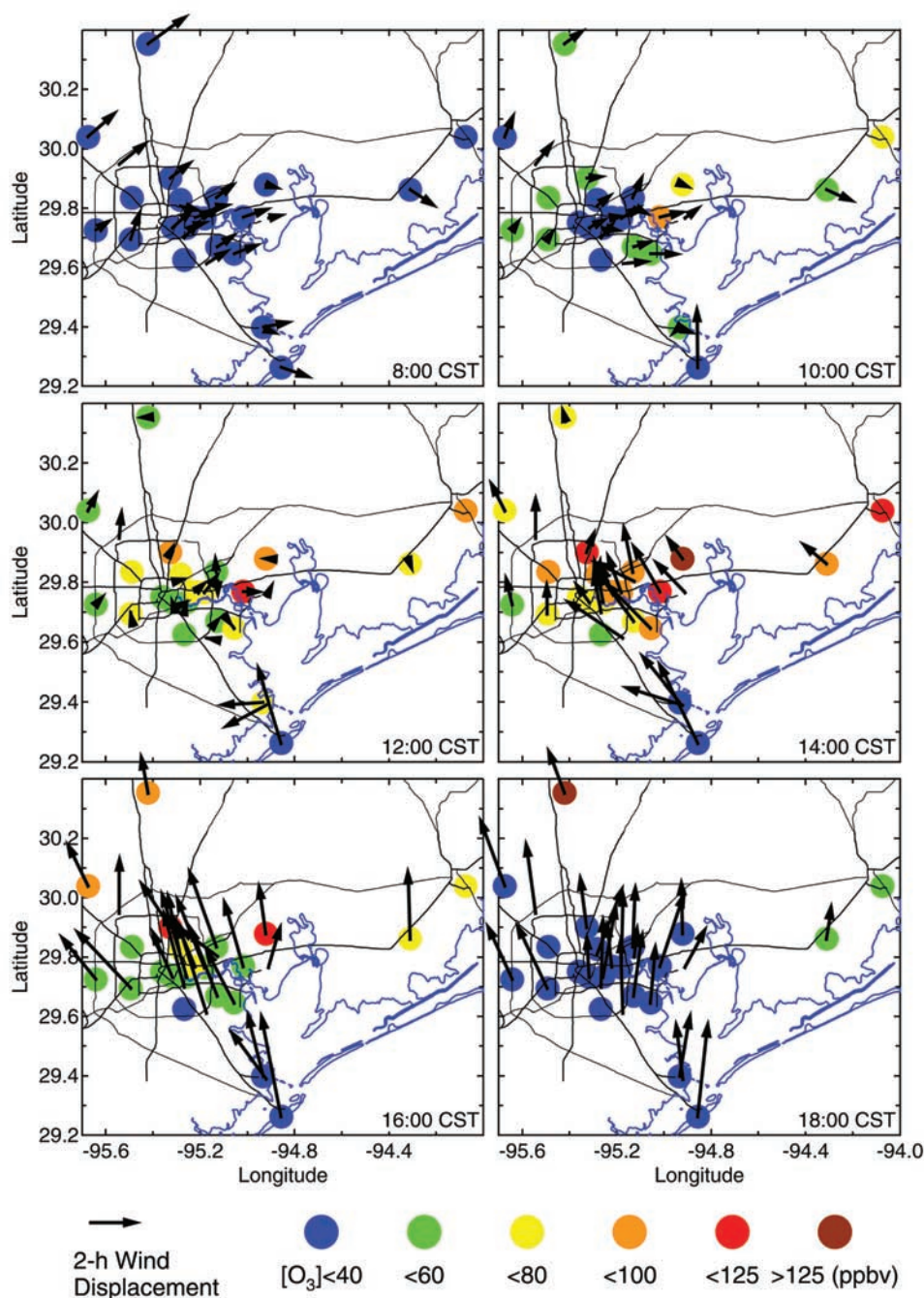


Figure 3. Ozone concentrations measured in the surface network surrounding Houston on 29 August 2000. Ozone concentrations color coded according to value. Ozone concentrations are averages for the 2 hours subsequent to the times shown in the part figures. Length of the arrows indicates the travel distance for the subsequent 2 hours as computed from locally measured surface winds. Note that O₃ concentrations remain at modest levels throughout the day except for a few sites north of the Ship Channel.

[14] The midday Twin Otter Flight and the afternoon G-1 flight both indicated a geographic distribution for O₃ (Figures 2b and 2c) similar to the distribution observed during the morning G-1 flight. Low background concentrations were observed at all locations except for the region to the east of Houston and to the north of Galveston Bay. While it appears that this area of high O₃ concentrations filled in over the duration of the three aircraft flights, essentially the

same area of high O₃ concentration that formed during the late morning persisted throughout the day. Although peak O₃ increased, the approximate area covered by this region of high O₃ was at most 50 km long and 10–20 km wide.

[15] A geographic representation of the NO_x concentrations measured by the G-1 during the morning flight is shown in Figure 4. NO_x concentrations were high over central Houston and the industrialized region to the east but

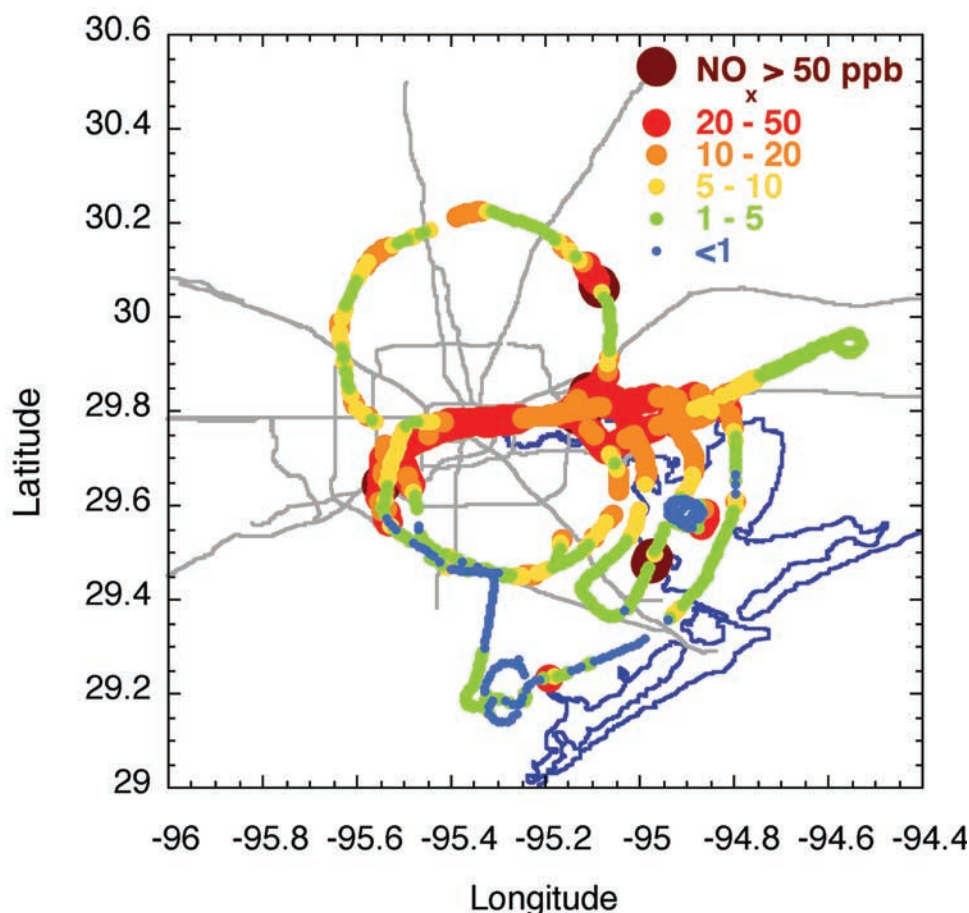


Figure 4. Geographic distribution of NO_x concentrations measured on the morning flight of the G-1 showing the accumulation of NO_x over downtown Houston and to the north of the Houston Ship Channel.

were fairly low elsewhere. This distribution is consistent with the traffic density in the area and with the location of significant NO_x point sources to the southwest (Parrish Power Plant located just to the SW of the city at latitude/longitude of 29.54°/95.78°) and to the east of the city. Despite the difference in NO_x sources, there appears to be no significant difference between NO_x concentrations observed over downtown Houston and those over the Ship Channel (i.e., maximum values were both circa 50 ppb). The high NO_x concentrations observed are also consistent with the relatively undeveloped mid- to-late morning boundary layer which constrained emissions to a layer less than 1 km in depth. Measurements were also made prior to peak photochemical hours so that NO_x had not yet had sufficient time to react. The geographic distribution of NO_x concentrations observed during the afternoon flight (not shown) was very similar to the morning distribution, except that the concentrations were much lower. This may be attributed principally to dilution by the growing boundary layer and chemical reaction.

[16] Figure 5 shows the geographic distribution of the hydrocarbon OH reactivity for all of the hydrocarbon canister samples collected on the three aircraft flights. For purposes of Figure 5, oxygenated species such as CO and HCHO and terpenes are not included in the calculation of the reactivity. These species were omitted to make the

hydrocarbon data from the two aircraft compatible since the Twin Otter did not have HCHO and CO measurements and the terpene measurements on the G-1 were thought to be unreliable. Most of the hydrocarbon OH reactivity rate constants needed to compute the hydrocarbon reactivity come from the work of *Atkinson* [1994]; rate constants not listed by *Atkinson* [1994] were estimated from the work of *Kwok and Atkinson* [1995]. Although sparsely determined, the geographic distribution of hydrocarbon reactivity is much different than observed for NO_x. The data clearly indicate that there are samples collected north of the Ship Channel exhibiting hydrocarbon reactivities that are as much as three to five times higher than those observed either over downtown Houston or the surrounding area. These differences in the geographic distribution of NO_x and hydrocarbon reactivity indicate that the VOC/NO₂ reactivity ratio is very different over downtown Houston than it is over the industrial area. As will be shown below, this difference has a major effect on the rate and efficiency of ozone formation in the two areas.

[17] Formaldehyde measurements were made on the G-1 for the morning flight and for a portion of the afternoon flight but were not made on the Twin Otter. The geographic distribution of the HCHO measurements from the morning G-1 flight is shown in Figure 6. Concentrations in the area surrounding Houston and over downtown Houston were all

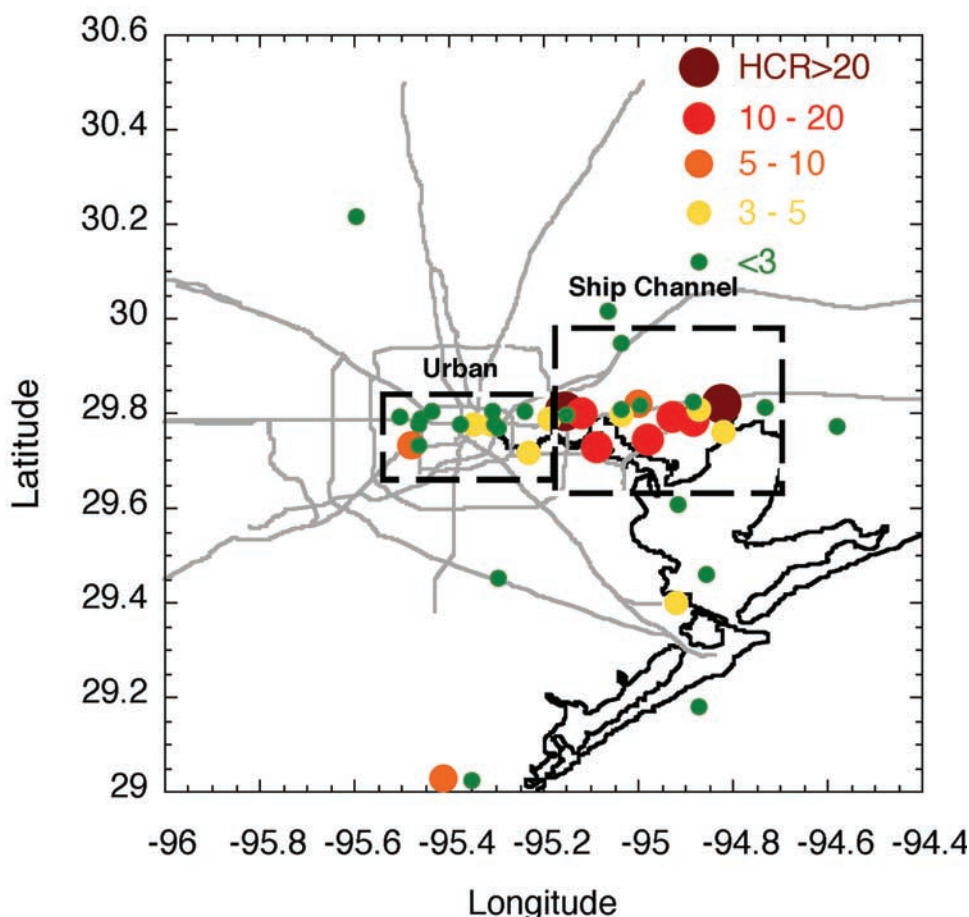


Figure 5. Geographic distribution of hydrocarbon OH reactivity measured on the three aircraft flights of 29 August 2000 showing much higher reactivities in the region labeled “Ship Channel” than in the area labeled “Urban.” Estimates of hydrocarbon reactivity shown in the figure do not include contributions from CO, HCHO, or other oxygenated hydrocarbons, or terpenes.

less than 5 ppb. Over the Ship Channel, however, concentrations were generally quite high, reaching a maximum value of nearly 25 ppb. Concentrations of this magnitude are the highest we have observed in the study of five major metropolitan areas in the United States [Lee *et al.*, 1998; Kleinman *et al.*, 2002]. It is important to note that the geographic pattern exhibited by HCHO is very similar to the one exhibited by O₃. As will be shown below, this is consistent with the mixture of hydrocarbons that are principally responsible for formation of the O₃ plume that was observed during the flight and as well with the importance of formaldehyde photolysis as a source of primary radicals that drive the O₃ formation process. Similar to morning flight, the geographic distribution of HCHO for the afternoon flight closely followed the distribution of O₃.

3.2. Apportionment of Hydrocarbon Reactivity

[18] For purposes of this analysis it is instructive to consider samples collected over the Ship Channel separately from those collected over Houston as the magnitude of the reactivities in these two geographical regions is distinctly different. The two areas of concern are indicated in Figure 5. The samples collected to the east of Houston over the industrialized area exhibit a broad range of reactivities, as shown in Figures 5 and 7a. Not quite 50% of the

industrial-area samples exhibit reactivities that are similar to those in the urban area (Figures 5 and 7b). The remaining 50% exhibit elevated reactivities, and it is to these samples that we turn our attention. Noteworthy for the high-reactivity samples is the importance of alkenes, which represent over 50% of the reactivity for seven of the eight samples exhibiting reactivities greater than 5 s⁻¹. For all of the high-reactivity samples, the most important alkenes are ethylene and propylene, but the relative importance of these two alkenes with respect to one another varies from sample to sample.

[19] For most of the urban samples, alkenes, alkanes, and biogenics contribute about equally to the hydrocarbon reactivity. For the four samples exhibiting the highest reactivity, alkenes contribute the most to the reactivity. This may be bleed over from the many alkene sources that are present in the Ship Channel or transport of alkenes from the industrial facilities to the south of Houston.

3.3. Comparison of Ship Channel and Urban Houston Measurements

[20] In order to more completely illustrate differences in O₃ formation over Houston and the industrial region to the east we now examine G-1 transects across downtown Houston and the Ship Channel during the late morning

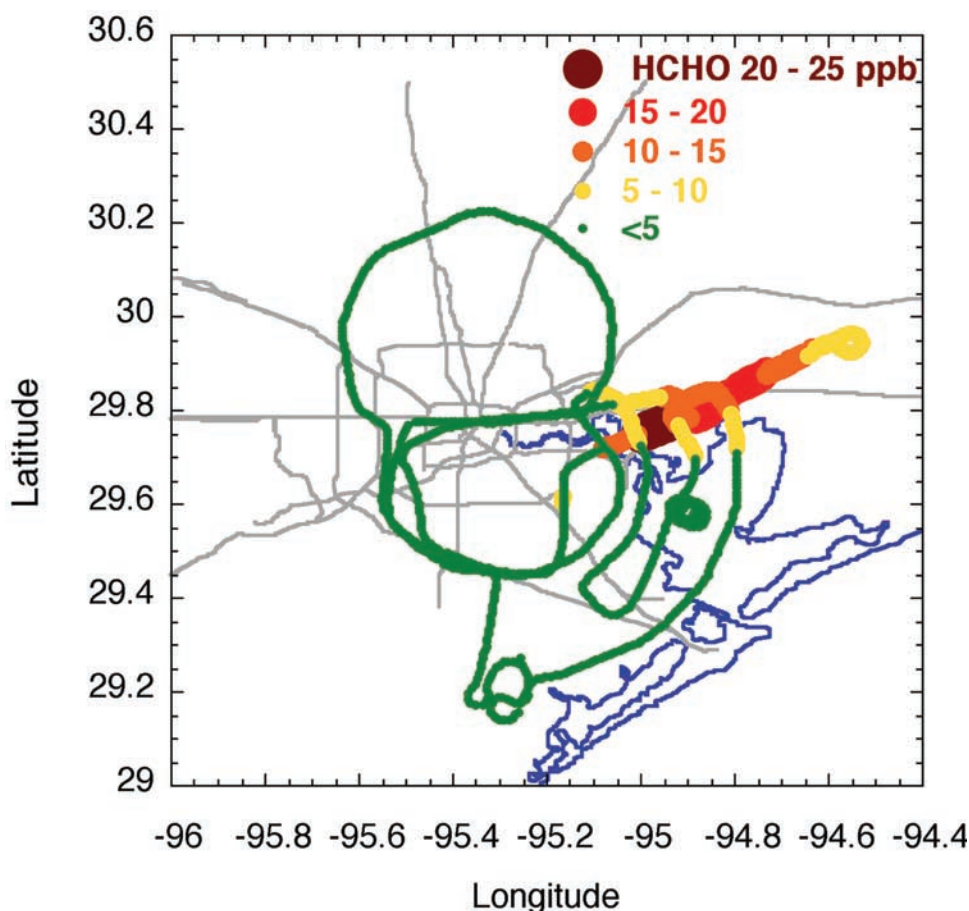


Figure 6. Geographic distribution of formaldehyde from the morning G-1 flight. Note the much higher concentrations of HCHO to the east of Houston.

and early and late afternoon. The timing and location of these transects allowed for both a comparative examination of the oxidant formation chemistry over the urban area and the industrial region and for documentation of the time evolution of this chemistry as the day progressed. Ground tracks are shown in Figure 8; downtown Houston is on the left side of the map, and the Ship Channel and Galveston Bay are on the right side of the map. Point sources of

hydrocarbon emissions clustered about the Ship Channel are indicated by the symbols. The first of these transects was made between circa 1040 and 1050 CST, the second between 1340 and 1356 CST, and the third between 1532 and 1549 CST.

3.3.1. Trace Gas Concentrations

[21] Trace gas concentrations and hydrocarbon reactivities measured during the three transects are shown in

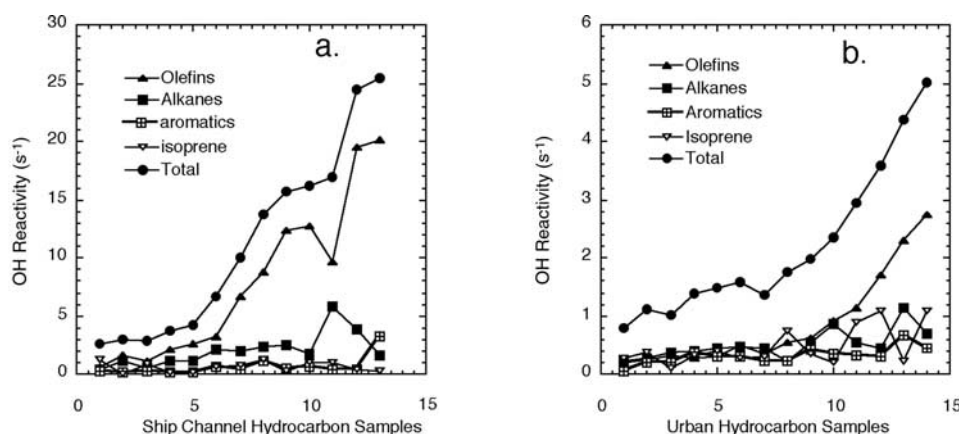


Figure 7. Comparison of the speciation of hydrocarbon samples in the areas designated (a) “Ship Channel” and (b) “Urban” in Figure 5. Samples ordered according to hydrocarbon reactivity. Oxygenated species such as CO and HCHO and terpenes are not included in calculation of reactivities.

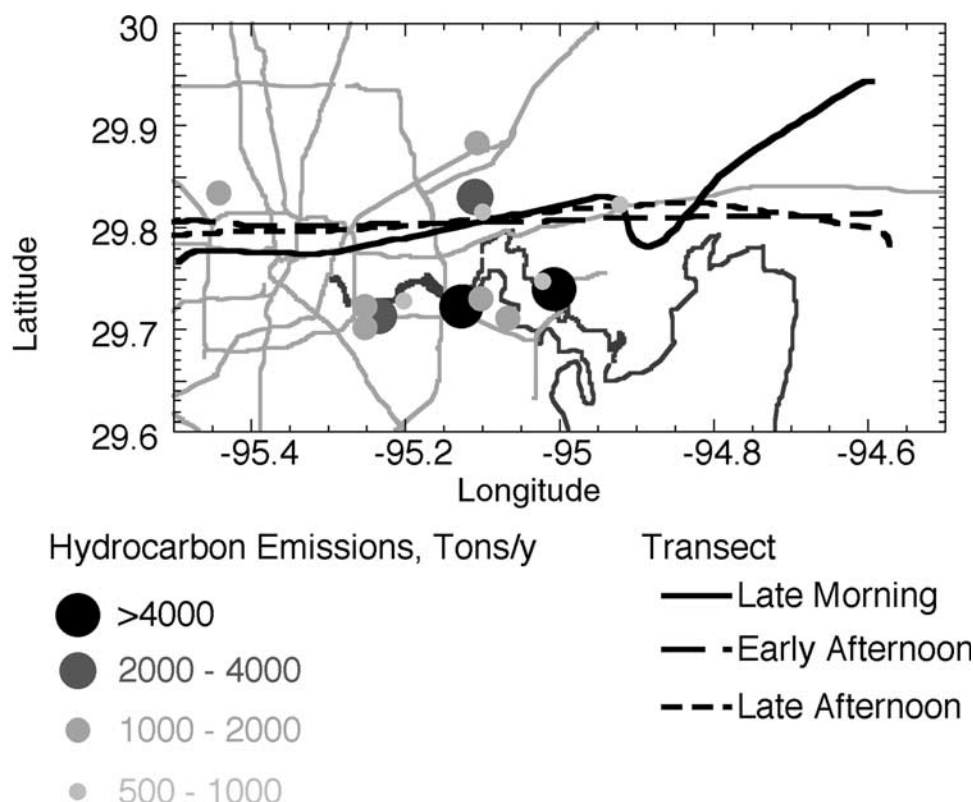


Figure 8. Ground tracks for G-1 transects made over the center of Houston and to the east over the Ship Channel industrial area. Circles indicate the strength of major sources of hydrocarbon emissions around the Ship Channel. Early and late afternoon transects are from the beginning and ending portions of the afternoon G-1 flight.

Figures 9–11. For Figures 9–11, hydrocarbon reactivities include contributions from CO and HCHO. Concentrations are plotted as a function of longitude to facilitate, in conjunction with Figure 8, identification of the geographical location of major features of these plots. Figures 9a, 10a, and 11a show the ozone concentrations measured during the three transects. The most striking feature of these plots is the persistent difference between the ozone concentrations measured over downtown Houston and those measured over the industrial area to the east observed throughout the day. Ozone concentrations over the urban area are just over 30 ppb during the morning flight, increase to about 65 ppb by early afternoon, and to nearly 80 ppb by late afternoon. Ozone concentrations over the urban area during the morning flight have certainly been influenced by other sources, as indicated by the observation of a fairly large SO₂ peak (Figure 9b) on the west side of the urban area, which probably comes from the Parrish Power Plant located to the SW of the city. The influence of such point sources on the urban area seems to be somewhat less during the afternoon. Ozone concentrations to the east over the industrial area are much higher than the urban area (by as much as 80 ppb), and this difference is maintained throughout the day, with peak concentrations over the industrial area reaching 180 ppb by late afternoon. The area of elevated O₃ concentration over the Ship Channel is not monolithic but seems to be a mixture of plumes from separate sources.

[22] NO_y and NO_x concentrations are the highest over both the urban and industrial areas during the morning flight

(Figure 9). Over the urban area, almost all of the NO_y is present as NO_x, indicating little reaction, and as observed, very little in the way of O₃ formation relative to background. Toward the east, a plume of high NO_y and NO_x is encountered, and further to the east, both NO_y and NO_x concentrations decrease, and the fraction of NO_y present as NO_x decreases. The peak O₃ concentration of 130 ppb is associated with a NO_x/NO_y ratio of about 0.5. NO_x and NO_y concentrations and the fraction of NO_y present as NO_x decrease over the urban area during the remaining two flights of the day (Figures 10 and 11) due to dilution by the growing boundary layer and in the case of NO_x due to reaction. During the first afternoon flight, NO_y and NO_x concentrations in the industrial area are lower than during the morning flight and a much smaller fraction of NO_y is present as NO_x. During late afternoon, NO_y concentrations over the industrial area are similar to those observed earlier in the afternoon except for the presence of some fairly high NO_x plumes that appear to be freshly emitted. Near the eastern end of the transect, a photochemically mature region of high O₃ is observed containing NO_x concentrations of less than 2 ppb.

[23] Figures 9b, 10b, and 11b show the SO₂ and formaldehyde concentrations. The variation of SO₂ along the flight tracks is very complex due to the multiplicity of SO₂ sources around the Ship Channel and elsewhere in the area. At some locations these SO₂ peaks appear to be correlated with peaks in the NO_y, NO_x, and or O₃ concentrations, in other instances there appears to be no relation between SO₂ and the concentrations of other species that were measured.

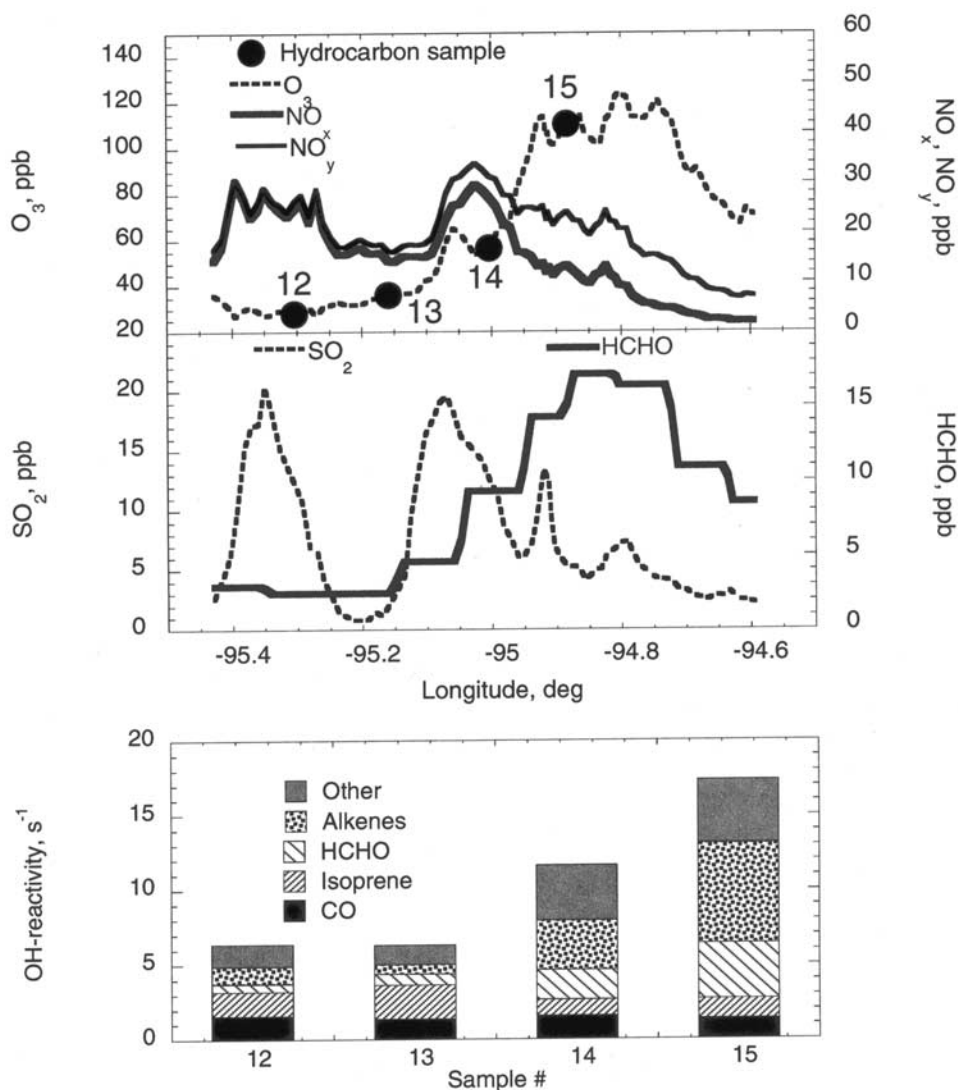


Figure 9. Trace gas concentrations and hydrocarbon reactivities measured during the 29 August 2000 late morning G-1 transect depicted in Figure 8.

[24] During the morning flight, formaldehyde concentrations were ~ 2 ppb over the city but increased to the east to a maximum of about 18 ppb and were strongly correlated with oxidant concentrations (Figures 9b and 11b). This correlation between formaldehyde and oxidant concentrations strongly suggests that the low molecular weight alkenes, ethylene and propylene, were significant contributors to the hydrocarbon reactivity involved in generating the high ozone that was observed. Formaldehyde measurements were not available for the early afternoon transect. For the late afternoon transect, formaldehyde concentrations are again low over the city and exhibit a peak to the east, downwind of the industrial source region. The correlation between O₃ and HCHO is not as good as for the morning transect because the afternoon O₃ plume is more photochemically aged, causing the relationship between formaldehyde and O₃ to be lost as formaldehyde reacts with OH or is photolyzed producing peroxy radicals and CO.

[25] Figures 9c, 10c, and 11c show the hydrocarbon reactivity apportioned into five categories. The locations of the samples are indicated by the dots and sample

numbers superimposed on the plots of the ozone shown in Figures 9a, 9b, and 9c. Samples 12 and 13 collected over the center of the Houston urban region during the morning flight (Figure 9) exhibit reactivities similar to those we have observed in other urban areas [Kleinman *et al.*, 2002]. For both samples, approximately 90% of the reactivity is fairly evenly split between nonmethane nonisoprene hydrocarbons (NMNIHC), isoprene, and CO. The two samples collected to the east exhibit much higher reactivities (by a factor of 2–3) and an apportionment that reflects the importance of alkenes emitted by industries in the area and their photodegradation products, as indicated by the fraction of the reactivity contributed by HCHO.

[26] Hydrocarbon reactivities measured across the region during the two afternoon flights, shown in Figures 10 and 11, were on average lower than the morning flight. For samples collected over the urban area, this reflects both reaction and dilution. The same factors affect the Ship Channel samples, but in addition, hydrocarbon sampling is sparse, and near major point sources, sampling is a hit-or-miss proposition. Nonetheless, both afternoon transects

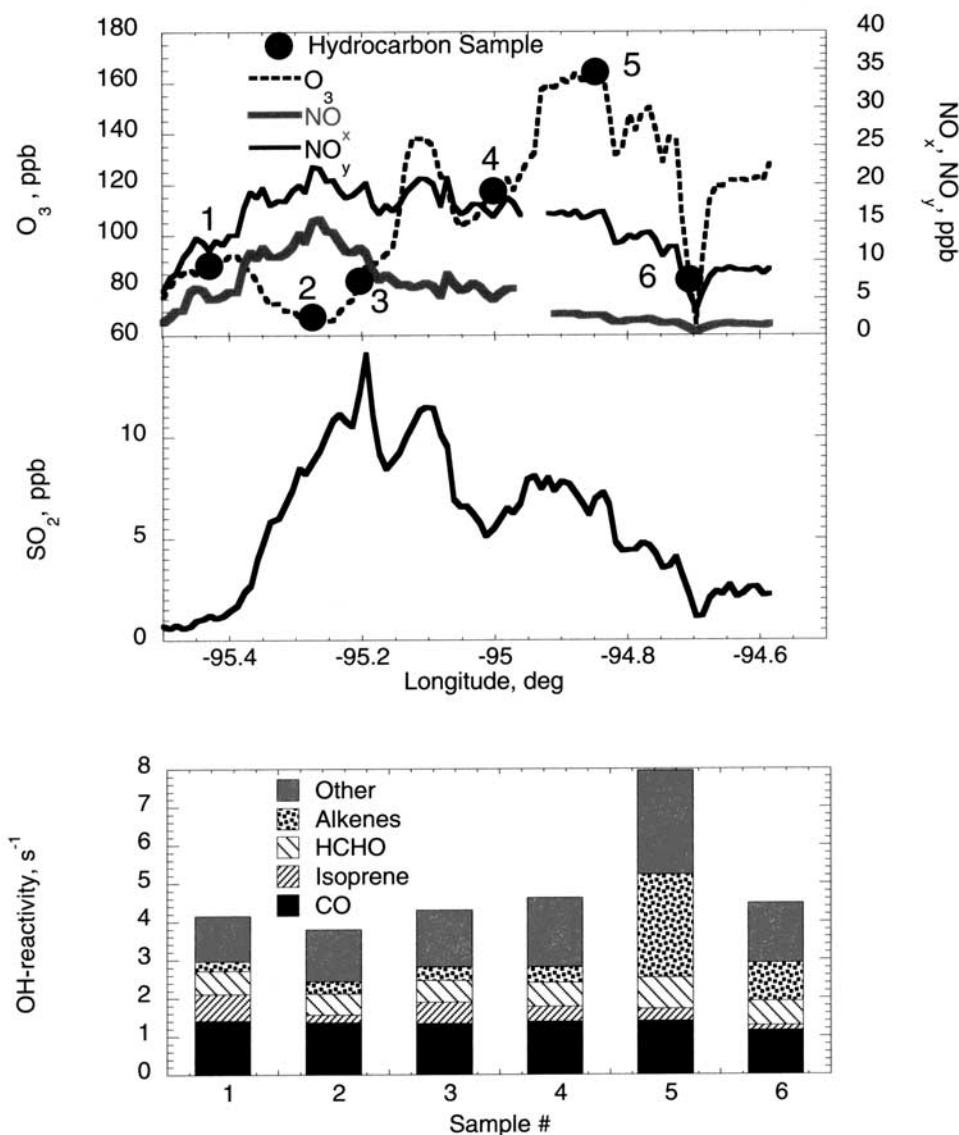


Figure 10. Trace gas concentrations and hydrocarbon reactivities measured during the 29 August 2000 early afternoon transect of the G-1. Gaps in the trace gas concentrations are due to instrument zeroes.

exhibit individual samples with high alkene reactivity, and for the last transect, high concentrations of the product species HCHO, indicating that at some time in the history of the air mass, hydrocarbon reactivities had been high and probably dominated by low molecular weight alkenes. It is noteworthy that hydrocarbon reactivities in the mature O₃ plume to the east (Figure 11) were fairly low, indicating extensive consumption by chemical reaction during O₃ formation.

3.3.2. Ozone Production Efficiencies

[27] Figure 12 shows a comparison of the ozone production efficiency with respect to NO_x for the Houston urban and Ship Channel plumes derived from regression analysis of O_x (NO₂ + O₃) and NO₂ (NO₂ is defined as NO_x oxidation products which are principally HNO₃ and peroxyacetylnitrate (PAN)) measurements. Figure 12a compares production efficiencies in the urban and industrial plumes observed during the late morning transect (Figure 9). Figure 12b compares the efficiencies during

the late afternoon transect (Figure 11). The industrial plumes at the east end are compared to the urban plume at the west end for both late morning (Figure 12a) and late afternoon (Figure 12b) transects.

[28] The efficiency in the urban area during the morning flight is very low (0.5) and ill defined (± 1) because so little O₃ has formed (Figure 12a). This is typical of urban centers dominated by vehicle emissions during the late morning since the VOC/NO_x emissions ratio of vehicles is typically low and this causes O₃ formation to be slow and inefficient as both the instantaneous formation rate and efficiency are proportional to the hydrocarbon to NO₂ reactivity ratio [Daum *et al.*, 2000a, 2000b; Kleinman *et al.*, 2002]. In contrast, significant O₃ has already formed in the industrial plume, and this formation has occurred at an efficiency that is much higher than ordinarily observed in an urban plume. Since NO_x concentrations in this industrial plume are not significantly different than observed over urban Houston (Figure 9) but hydrocarbon reactivity is, it must be concluded

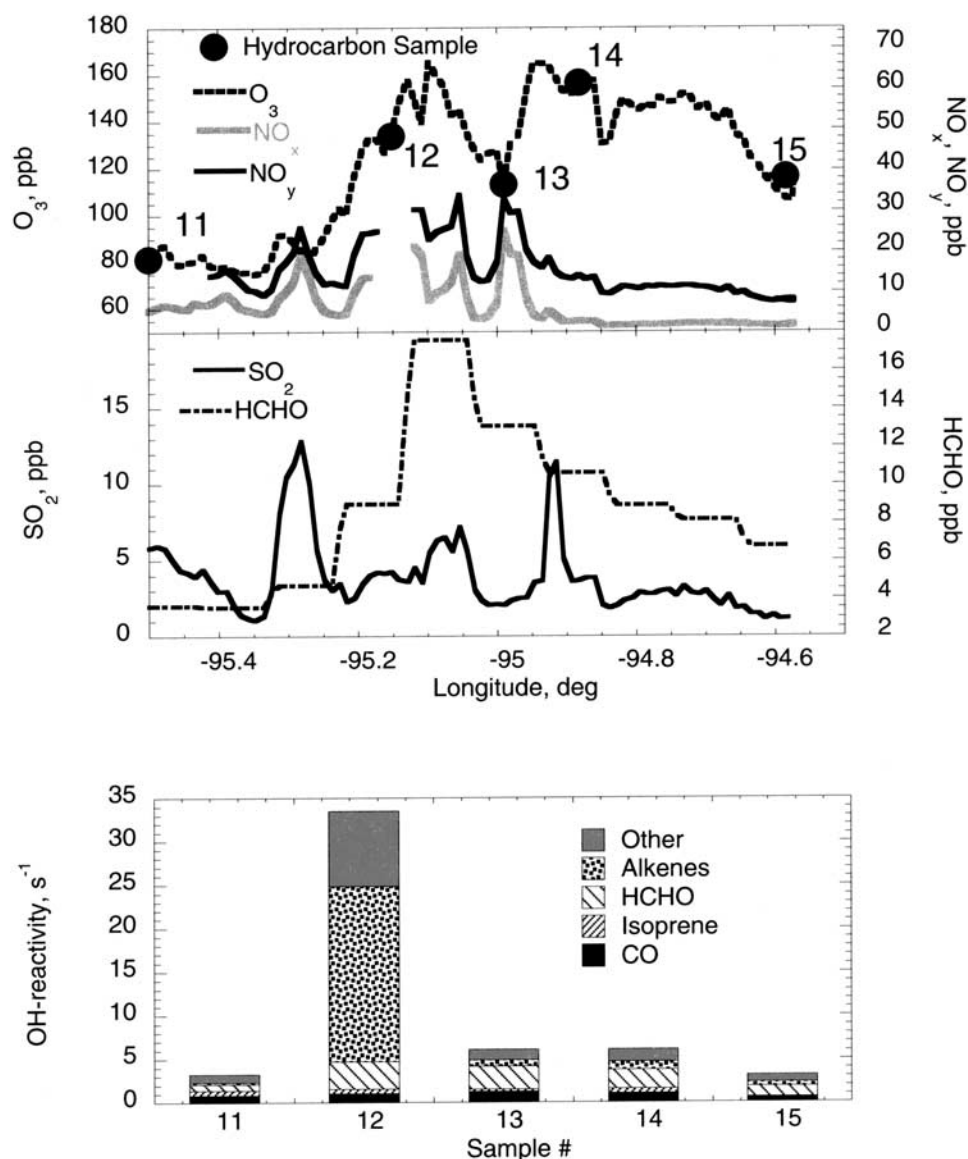


Figure 11. Trace gas concentrations and hydrocarbon reactivities measured during the 29 August 2000 late afternoon transect of the G-1. Gaps in the trace gas concentrations are due to instrument zeroes.

that the observed difference in efficiency of O₃ formation is a consequence of the hydrocarbon to NO₂ reactivity ratio.

[29] Geographical differences in the efficiency of O₃ formation observed in the late afternoon are not nearly as large as they were during the late morning. The efficiency over the urban area has increased to about 5, which is typical for urban plumes in the late afternoon [Nunnermacker *et al.*, 1998; Daum *et al.*, 2000a, 2000b; Kleinman *et al.*, 2002], and the efficiency in the mature industrial plume has risen to 10.9. The increase in the urban plume efficiency is due to dilution and due to consumption of NO_x, both of which serve to increase the VOC to NO₂ reactivity ratio, which, in turn, increases the O₃ formation efficiency.

3.4. Back Trajectories

[30] To understand the precursor sources that led to the preferential accumulation of high concentrations of O₃

over the Ship Channel in comparison to the Houston urban center on 29 August, we examine back trajectories along the three east-west transects shown in Figure 8 and discussed in Section 3.3. These back trajectories at flight altitudes were computed using gridded wind fields generated from the wind profiler network deployed during the program. Figure 13a shows back trajectories corresponding to the four hydrocarbon samples collected on the morning transect. Time between the markers on the trajectories represents 1 hour. It is clear from these trajectories and by reference to Figure 8 that the urban area was unaffected by the point sources clustered about the Ship Channel as the trajectories indicate that transport was from the SSW, where there are few point sources of either NO_x or VOC, with the exception of the Parrish Power Plant located to the SW of Houston. Thus it may be concluded that trace gas composition measured over downtown Houston primarily reflects typical urban emis-

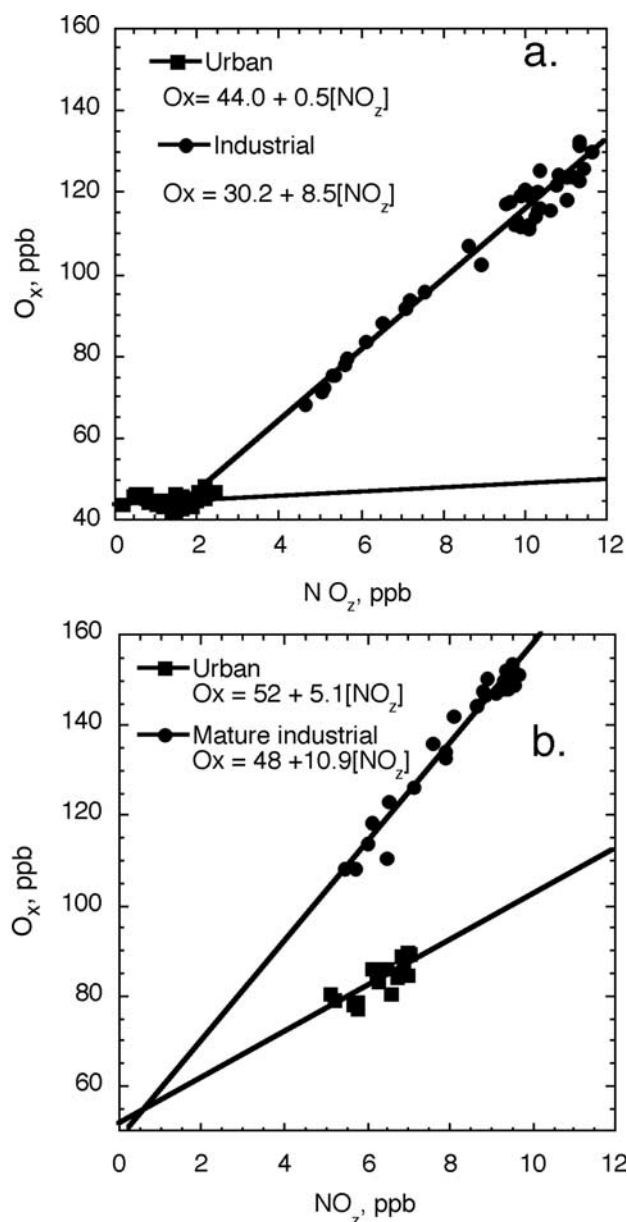


Figure 12. Comparison of integrated ozone production efficiencies for the urban and Ship Channel plumes: (a) late morning G-1 transect and (b) late afternoon G-1 transect.

sions and to the east reflects point sources clustered about the Ship Channel.

[31] The pattern of back trajectories during the two afternoon transects (Figures 13b and 13c) is very similar to the pattern exhibited by the morning trajectories. Back trajectories with starting points over the urban center passed to the southwest of Houston over relatively source-free areas, whereas back trajectories from samples collected to the east of Houston passed over the Ship Channel source region. The afternoon back trajectories also indicate a period of very low wind speeds, as indicated by the close spacing of the 1-hour time markers on the trajectories. This period of low wind speeds allowed the accumulation of emissions in the source region surrounding the Ship Channel and can be directly linked to the high concentrations of

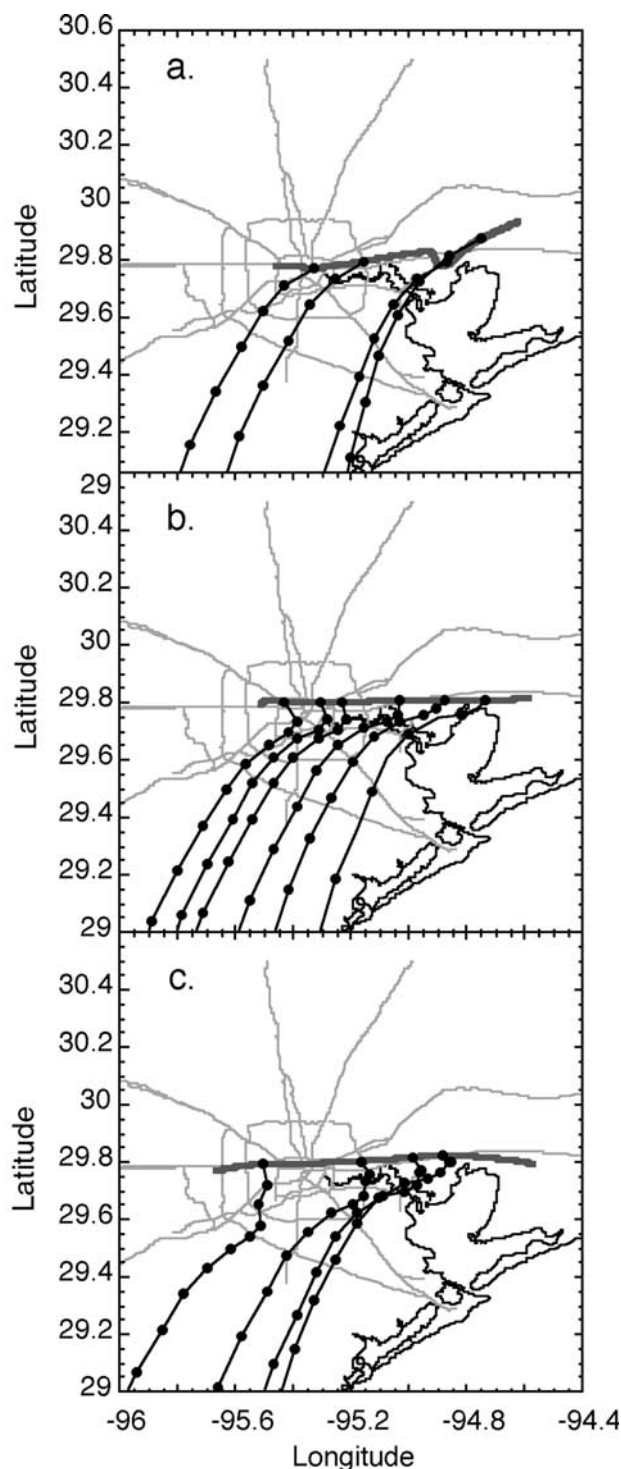


Figure 13. Back trajectories for hydrocarbon samples collected during the three G-1 transects of the Houston area depicted in Figures 9–11: (a) morning, (b) early afternoon, and (c) late afternoon transects. Trajectories indicate that samples collected over downtown Houston were not affected by emissions from the industries surrounding the Ship Channel.

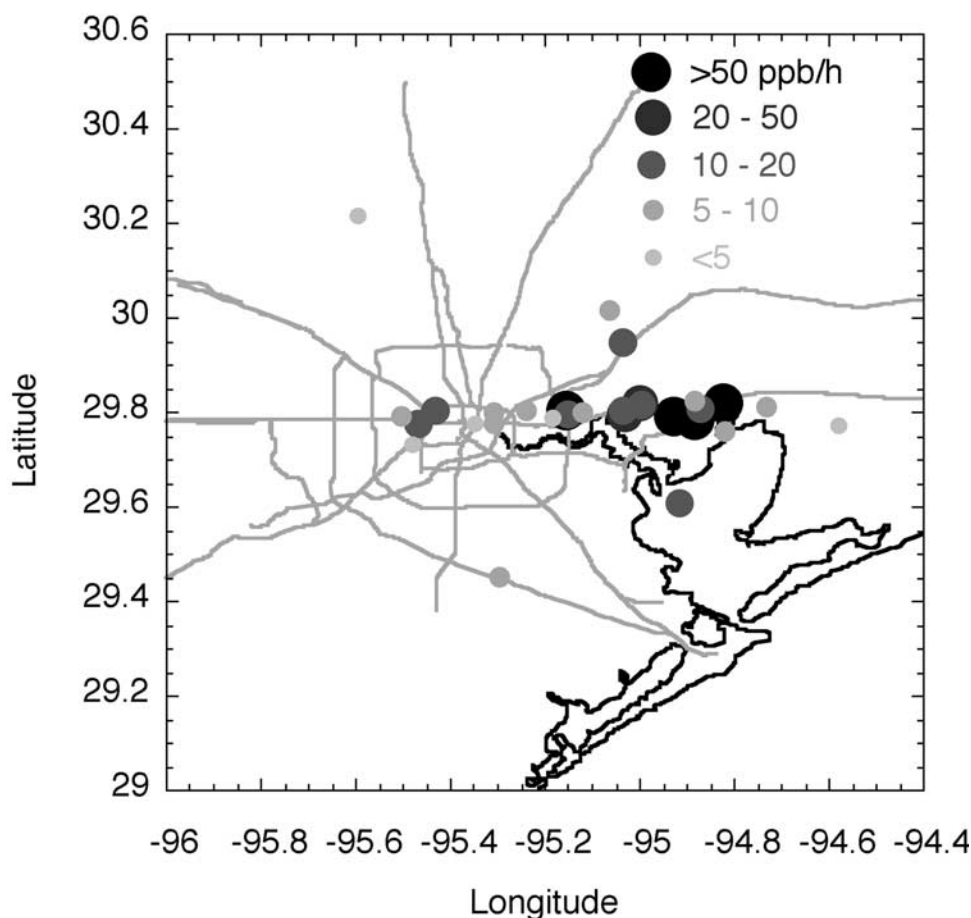


Figure 14. Geographic distribution of the instantaneous ozone formation rates, $P(O_3)$, computed using a box model constrained by observed concentrations of stable species. Formation rates correspond to hydrocarbon canister samples collected by the G-1. Note the high formation rates in the vicinity of the Ship Channel.

both primary species and O₃ that were observed during the aircraft flights.

3.5. Instantaneous Ozone Formation Rates and Efficiencies

[32] Characteristics of ozone formation were examined using a box model constrained by observed concentrations of NO_x, HC, and other stable species; details of these calculations are described elsewhere [Kleinman *et al.*, 2000, 2001, 2002, and references therein]. The number of calculations corresponds to the number of hydrocarbon samples that were collected. The number of calculations was further limited to data collected by the G-1, as an insufficient number of species were measured on the Twin Otter to adequately constrain the calculations.

[33] Figure 14 shows the geographic distribution of the instantaneous ozone formation rate ($P(O_3)$, ppb/h) calculated for all of the hydrocarbon samples collected during the two G-1 flights. An obvious feature of the geographical distribution of $P(O_3)$ is that the highest values, a number of which exceed 50 ppb/h, are observed to the east of Houston and to the north of Galveston Bay. In contrast, formation rates over downtown Houston are mostly very low and never exceed 20 ppb/h. This difference in formation rates provides at least a

partial explanation of the reason why high ozone concentrations have accumulated over the Ship Channel and not over downtown Houston.

[34] The cause of the high formation rates to the east of Houston relative to downtown Houston is addressed in Figure 15, which shows some contrasting features of O₃ formation between the urban and industrial areas. Figures 15a–15c show $P(O_3)$, the NO_x concentration, and the hydrocarbon reactivity, respectively, for the six hydrocarbon samples collected east of Houston that exhibited $P(O_3)$ in excess of 20 ppb/h and for the seven samples collected directly over the urban center. The data in these plots have been ordered by $P(O_3)$. Aside from the obvious difference in the formation rates, the most striking difference between the two sets of samples is the hydrocarbon reactivities. Four of the seven urban samples exhibit hydrocarbon reactivities that are less than 5 s⁻¹; the remaining three samples exhibit reactivities that are between 5 and 10 s⁻¹. For the Ship Channel samples, hydrocarbon reactivities range from just under 10 s⁻¹ to approximately 35 s⁻¹ and average about a factor of 4 higher than the urban samples. Since the NO_x concentrations over the urban area are about the same as they are over the Ship Channel (Figure 15b), it is reasonable to attribute the

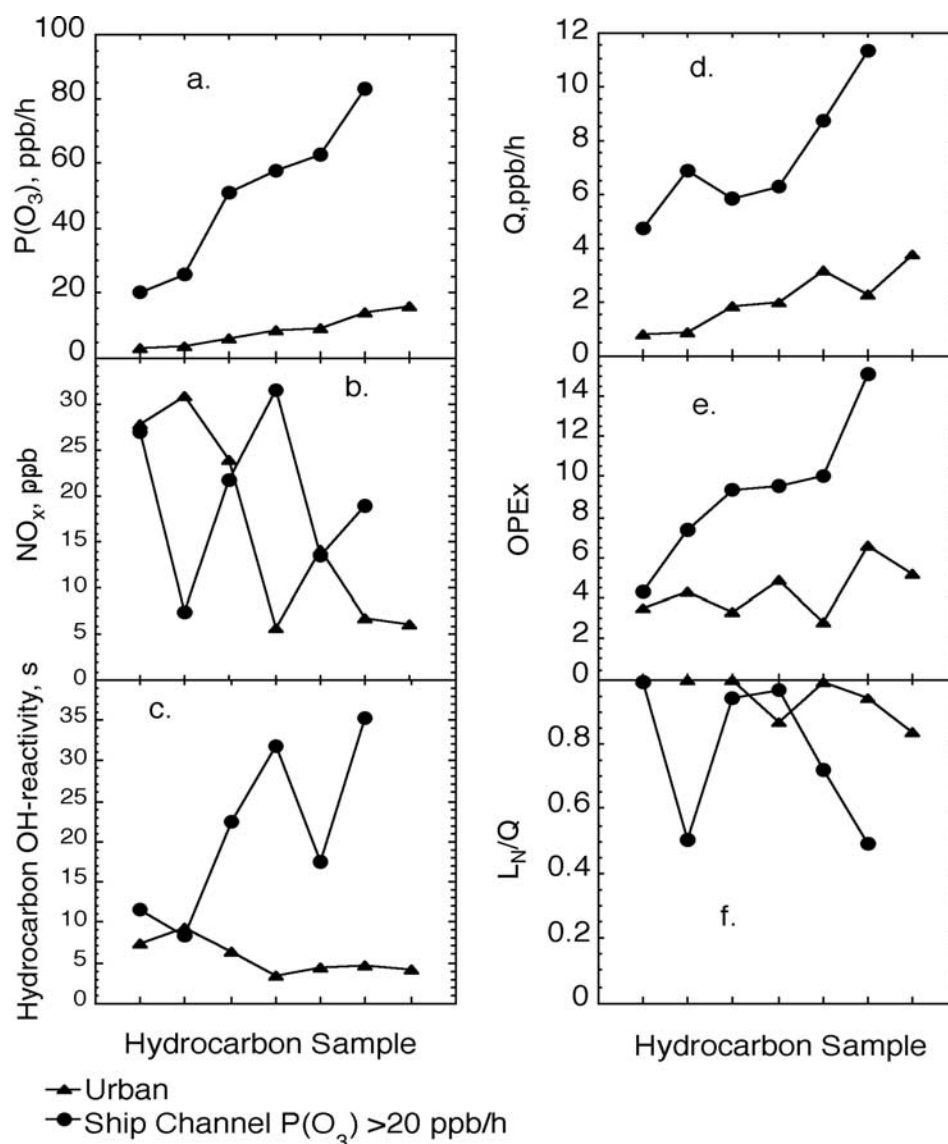


Figure 15. Comparison of the characteristics of O₃ formation in the Ship Channel to those in the Houston urban center. Ship Channel samples restricted to those exhibiting $P(O_3)$ in excess of 20 ppb/h. Each calculation corresponds to a hydrocarbon canister sample. Data include samples from both morning and afternoon flights.

enhanced $P(O_3)$ over the Ship Channel to the much higher hydrocarbon concentrations since to a first approximation, ozone formation rates at these NO_x levels are proportional to the VOC/ NO_2 reactivity ratio times the primary radical production rate [Daum *et al.*, 2000a, 2000b].

[35] Figure 15d compares the primary radical production rate Q for the two sets of samples. This quantity is important because radicals are the initiators of the O₃ formation process and the rate at which they are formed is linearly related to the rate of O₃ formation under hydrocarbon-limited conditions. Q is a function of the solar intensity and the concentration of O₃ and HCHO which upon photolysis form radicals that initiate O₃ formation. Radicals can also be formed by reaction of O₃ with alkenes. Figure 15d clearly shows that the primary radical production rate in the urban area is lower than it is in the Ship Channel by as much as a factor of 3. The reason for this

difference can be understood by reference to Table 1. For both urban and Ship Channel samples, the primary source of radicals is photolysis of O₃ and formaldehyde. The flux of radicals coming from O₃ photolysis in the urban samples is circa 50% of what it is in the Ship Channel samples because the O₃ concentration is only half as high. The flux of radicals arising from HCHO photolysis is more than four times as large in the Ship Channel samples as it is in the urban samples because the HCHO concentration is about a factor of 4 higher; the fraction arising from HCHO photolysis also represents a larger fraction of the total radical production. The fraction of radicals termed “other” is also higher for the Ship Channel samples because of the high alkene concentrations, which upon reaction with O₃ can also result in the generation of a significant radical flux.

[36] Figure 15e shows that there is also a difference in the efficiency of ozone production (defined as the ratio of

Table 1. Comparison of Primary Radical Production Ship Channel Versus Urban Houston^a

Parameter	Ship Channel, P(O ₃) > 20 ppb/h	Urban Houston
<i>Q</i> (total), ppb/h	7.3	2.1
<i>Q</i> (O ₃), ppb/h	2.8	1.3
<i>Q</i> (HCHO), ppb/h	2.4	0.5
<i>Q</i> (other), ppb/h	2.1	0.3
O ₃ , ppb	102	49
HCHO, ppb	14.4	2.5
Ethylene, ppb	14.0	1.9
Propylene, ppb	5.6	0.4

^aData represent averages of the six Ship Channel and seven urban samples referred to in the text.

the ozone formation rate divided by the rate of nitric acid formation) between the urban and industrial samples. For the Ship Channel samples these efficiencies vary between just under 5 to more than 12 ppb O₃/ppb HNO₃. In contrast, the urban samples ranged between approximately 3.5 and 6. On average, the efficiency between the two sets of samples differed by nearly a factor of 2. The O₃ formation efficiency in the Ship Channel samples is again a consequence of the high hydrocarbon reactivity, as to a first approximation this efficiency is proportional to the ratio of the hydrocarbon to NO₂OH reactivity [e.g., Daum *et al.*, 2000a, 2000b; Kleinman *et al.*, 2002].

[37] Figure 15f shows that the P(O₃) for the Ship Channel samples varies between hydrocarbon-limited and close to NO_x-limited behavior, as indicated by the quantity L_N/Q , which represents the fraction of radicals that are being removed from the ozone formation cycle by formation of HNO₃. If L_N/Q is less than 0.50, the instantaneous chemistry is limited by the availability of NO_x and otherwise by the availability of hydrocarbons [Kleinman *et al.*, 1997, 2001; and references therein]. This quantity is expected to vary in the Ship Channel because the hydrocarbon and NO_x emissions are not necessarily collocated and because NO_x disappears from the system more rapidly than do hydrocarbons. The urban samples, by contrast, are all strongly hydrocarbon limited, as is characteristic of most large urban areas in the United States.

[38] This view of the instantaneous chemistry gives important insight as to why O₃ has preferentially accumulated in the Ship Channel and not over urban Houston. The basic driving force for this accumulation is the high hydrocarbon reactivity originating from industries in the area. These additional hydrocarbons have a strong effect on both the rate and efficiency of O₃ formation as both the rate and efficiency are directly related to the hydrocarbon to NO₂ reactivity ratio. However, there are also more subtle effects that manifest themselves as an increase in the primary radical production rate, *Q*. The high hydrocarbon reactivity dominated by alkenes not only provides fuel for O₃ formation but a product of low molecular weight alkene oxidation is HCHO which, via photolysis, produces radicals that enhance P(O₃) and ultimately the O₃ concentration. The high O₃ concentration in turn enhances the rate of the O₃/alkene reactions, which also generate radicals that enhance the rate of O₃ production. This combination of factors can lead to the very rapid formation of high concentrations of O₃ as observed.

3.6. Hydrocarbon or NO_x Limitations to O₃ Formation

[39] An important question with respect to control strategies is whether the maximum amount of O₃ formed is limited by the availability of NO_x or hydrocarbons. The city of Houston itself, similar to most large urban areas in the country, exhibits hydrocarbon-limited O₃ chemistry in the near field. However, the question of whether O₃ is NO_x or hydrocarbon limited when produced from Ship Channel emissions is important from the perspective of developing a control strategy. The usual mechanism for addressing this question is a series of modeling calculations with different emissions scenarios. However, since hydrocarbon emissions from industries surrounding the Ship Channel are thought to be underestimated by as much as a factor of 10 or more in existing inventories, such an examination is not meaningful. Here we take an alternate approach and examine the photochemical product species distribution, specifically, the ratios $\Delta O_3/\Delta NO_z$, and *t*-peroxide/NO_z, where ΔO_3 and ΔNO_z are background corrected values of ozone and oxidized nitrogen species, respectively, and *t*-peroxide is the sum of H₂O₂ and organic peroxides. It has been shown that these ratios are fairly robust indicators of whether O₃ concentrations have been limited by the availability of NO_x or hydrocarbons [Sillman and He, 2002], a high value of these ratios indicating NO_x limited and a low value indicating hydrocarbon-limited O₃ formation. However, the values of the transition points between NO_x and hydrocarbon-limited chemistry vary from area to area [Sillman and He, 2002], and since they have not been determined for Houston, inferences regarding NO_x or hydrocarbon sensitivity will be discussed only in a relative sense in the following paragraphs.

[40] Differences between O₃ formation over downtown Houston and the Ship Channel industrial region are well illustrated by a G-1 transect of these two areas at circa 1400 CST. The flight track and some of the trace gas concentrations are shown in Figure 10. Figure 16a shows the O₃, NO_z, and total peroxide concentrations. Over the urban area, as indicated, NO_x concentrations are very high but O₃ concentrations are somewhat suppressed relative to adjacent areas; *t*-peroxide concentrations are nearly constant at about 3 ppb. The NO_x/NO_y ratio in this plume is about 0.5, indicating that there is significant potential for the formation of additional O₃. Several distinct O₃ plumes are observed to the east of the city. The narrow plume labeled SC-1 exhibits a peak O₃ concentration of nearly 140 ppb, but there is no corresponding peak in the NO_x concentration. The total peroxide concentration exhibits a small peak at the leading edge of this plume. The peak labeled SC-2, a composite of several smaller plumes, exhibits a peak O₃ concentration of circa 170 ppb; NO_x concentrations in SC-2 are 3 ppb and are small in comparison to the NO_y concentration (Figure 10), indicating a photochemically mature plume. The total peroxide concentration doubles from 4 to 8 ppb at the leading edge of this plume and increases at a slower rate thereafter.

[41] Figure 16b shows the variation of two indicator ratios $\Delta O_3/\Delta NO_z$ and *t*-peroxide/NO_z [Sillman and He, 2002] observed during this transect. Background ozone and NO_z concentrations required for calculation of ΔO_3 and ΔNO_z were estimated to be 60 and 3 ppb, respectively, from the “out-of-plume” G-1 data. Both indicator ratios are fairly low in the heart of the urban plume, but $\Delta O_3/\Delta NO_z$ goes up in

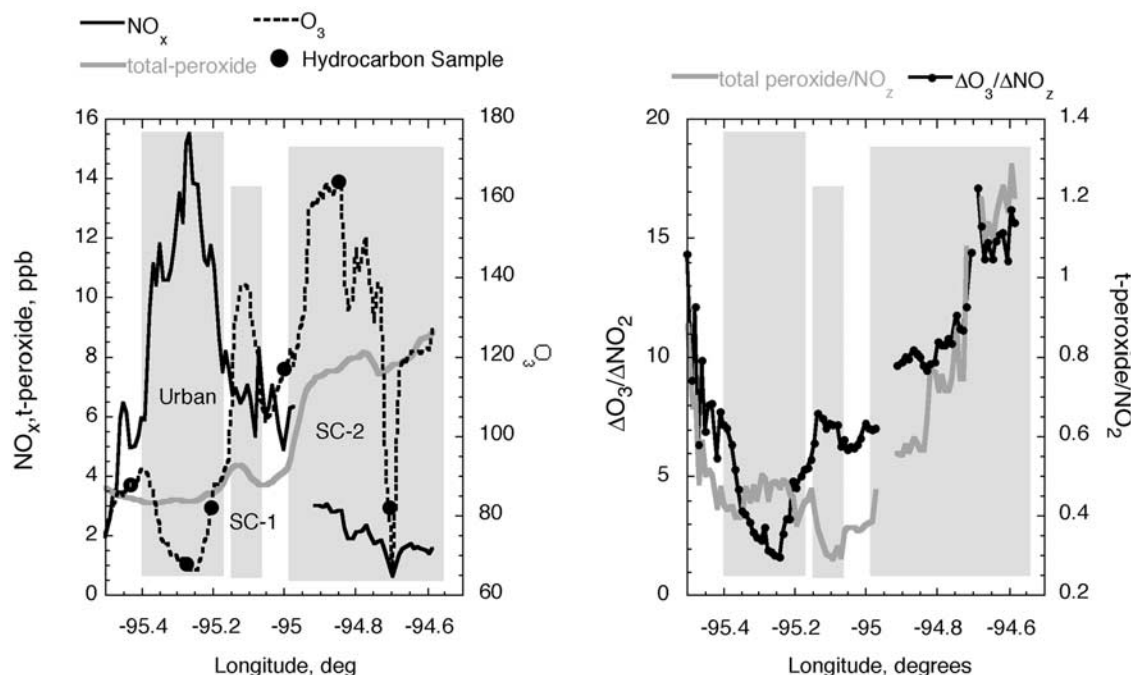


Figure 16. (a) Ozone, NO_x, and *t*-peroxide concentrations measured during the midafternoon transect of the Houston urban area on 29 August. (b) Ratio of *t*-peroxide/NO_z and ΔO₃/ΔNO_z, both indicating that O₃ formation over the urban area is much more hydrocarbon limited than in the mature plume over the Ship Channel.

SC-1 whereas *t*-peroxide/NO_z goes down. Both indicator ratios are much higher in the mature plume at the east end of the transect. In a qualitative sense, behavior of these indicator ratios suggests that O₃ formation in the Ship Channel plume is more NO_x limited than it is in the urban area. Although it is also obvious that NO_x/hydrocarbon sensitivity is a complex issue and such sensitivity may vary from plume to plume depending on the emissions and the composition of the air into which these emissions are mixed.

[42] It is also instructive to get a view of NO_x/hydrocarbon sensitivity from the instantaneous chemistry. However, it should be recognized at the outset that instantaneous chemistry gives only insight into what is happening at a point in time under prevailing conditions, whereas indicator ratios reflect the integration of what has happened during the entire O₃ formation process. Calculations made for each of the six hydrocarbon samples collected during the transect are given in Table 2. The location of the samples is shown in Figure 16a. It is clear from Table 2 that the instantaneous chemistry is consistent with the differences in O₃ formation chemistry inferred from the indicator ratios. For samples 2 and 3, collected in the heart of the urban plume, L_N/Q is very high, indicating that P(O₃) is hydrocarbon limited; samples 5 and 6 collected in the mature Ship Channel plume exhibit NO_x-limited O₃ formation. Sample 1 collected at the western edge of the urban area and sample 4 collected over the Ship Channel exhibit hydrocarbon-limited chemistry, but not as extremely as the urban samples. It is worth noting that P(O₃) in the mature Ship Channel plume (samples 5 and 6) is still appreciable and that O₃ formation is occurring very efficiently, as indicated by the high values of OPE_x shown in Table 2. In the absence of the input of any additional NO_x to this plume there is thus the potential for the efficient

formation of significant additional O₃ and such formation will be NO_x limited. In contrast, additional O₃ formation in the urban plume will be hydrocarbon limited until most of the NO_x has been depleted. The implications of the forgoing analysis for strategies for control of the Houston O₃ problem are not obvious. Clearly, O₃ formation in the Ship Channel region is more NO_x limited than it is in the urban area. However, it is also clear that the mix of sources in this region is very complex, and it would not be surprising to find that plumes from individual facilities imbedded within this region may differ with respect to NO_x or hydrocarbon sensitivity. From the data presented here it is also not possible to tell what would happen under meteorological conditions where emissions from the Ship Channel and urban areas are comingled, a situation where it is likely that very high concentrations of O₃ would be formed.

4. Summary and Conclusions

[43] Meteorological conditions on 29 August 2000 allowed a comparative study of ozone formation in the Houston urban plume and in the plume emanating from the

Table 2. Instantaneous Chemistry for the Early Afternoon G-1 Transect Depicted in Figure 10

Sample	Hydrocarbon Reactivity, s ⁻¹	NO _x , ppb	NO _x /NO _y	P(O ₃), ppb/h	L_N/Q	OPE _x
1	4.2	6.2	0.5	16.0	0.83	5.1
2	3.8	13.1	0.7	7.7	0.98	2.6
3	4.3	14.1	0.72	8.8	0.99	2.9
4	4.6	6.9	0.4	18.2	0.80	5.1
5	8.0	3.2	0.2	13.5	0.16	10.0
6	4.5	1.6	0.15	6.10	0.13	9.0

industrial complex clustered about the Houston Ship Channel east of downtown Houston. During the morning hours of 29 August, winds were light from the SSW carrying emissions to the NNE. From the middle of the day through late afternoon, a period of stagnation occurred, allowing accumulation of O₃ and product species separately over downtown Houston and over the Houston Ship Channel. A localized O₃ plume was observed to the east of the city, which by late afternoon exhibited concentrations of up to 200 ppb. In contrast, the maximum O₃ concentration observed over the urban area was 90 ppb. The biggest contrast between the two areas was observed during the late morning when O₃ concentrations over the city were only 40 ppb and in the industrial plume were in excess of 120 ppb. NO_x concentrations measured in the two plumes in the late morning were roughly the same, but hydrocarbon concentrations in the industrial plume were much higher, by as much as a factor of 10. In the industrial plume samples exhibiting the highest hydrocarbon reactivities, the low molecular weight alkenes, ethylene, propylene, and butenes contributed most to the reactivity. The industrial ozone plume also exhibited concentrations of HCHO, a photochemical degradation product of alkenes, of up to 25 ppb, whereas the maximum concentration over the urban area was less than 5 ppb. Back trajectories starting from downtown Houston and from the ozone plume observed to the east of Houston indicated that central Houston was not significantly affected by emissions from the many industrial sources in the area but the O₃ plume east of Houston had been.

[44] Photochemical box model calculations constrained by observations of temperature, water vapor, NO_x, hydrocarbons, O₃, and other stable species indicated that the instantaneous ozone formation rate in the industrial plume east of downtown Houston was much higher than in downtown Houston. Formation rates over downtown Houston ranged between approximately 3 and 18 ppb/h, whereas formation rates in the eastern industrial plume ranged between 3 and 80 ppb/h. Instances of high ozone formation rates in the industrial plume were driven by high concentrations of reactive hydrocarbons. Regions of high formation rates were also characterized by high formation efficiencies ranging up to 14 ppb O₃/ppb NO_x. Urban samples exhibited a maximum efficiency of circa 6.

[45] Ozone formation in downtown Houston, similar to most other urban areas in the United States, appeared to be limited by the availability of hydrocarbons. In contrast, ozone formation in the Ship Channel industrial plume appeared to be much less hydrocarbon limited, as indicated from the box model calculations and from analysis of the concentration ratios of photochemical product species. However, full-scale model calculations with realistic hydrocarbon emissions will be required to determine whether NO_x or hydrocarbon reductions would be most effective in controlling peak O₃ concentrations in the industrial plume.

[46] **Acknowledgments.** This study was supported by funding from the Department of Energy through the DOE Atmospheric Chemistry Program, U.S. Environmental Protection Agency through the Southern Oxidants Study, and by the Texas Commission on Environmental Quality. This research was performed under sponsorship of the U.S. Department of Energy under sponsorship of the U.S. DOE under contracts DE-AC02-98CH10886 and DOE FG02-98ER.

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C. M. Berkowitz, Atmospheric Sciences and Global Change Division, Pacific Northwest National Laboratories, MSIN K9-30, Richland, WA 99352, USA. (carl.berkowitz@pnl.gov)

P. H. Daum, L. I. Kleinman, Y.-N. Lee, L. J. Nunnermacker, and S. R. Springston, Environmental Sciences Department, Atmospheric Sciences Division, Brookhaven National Laboratory, Upton, NY 11973-5000, USA. (phdaum@bnl.gov; kleinman@bnl.gov; ynlee@bnl.gov; linden@bnl.gov; srs@bnl.gov)

J. Weinstein-Lloyd, Chemistry/Physics Department, State University of New York at Old Westbury, Old Westbury, NY 11568, USA. (lloydj@oldwestbury.edu)

J. Zheng, Institute for Terrestrial and Planetary Atmospheres, State University of New York at Stony Brook, NY, USA.